Photoexcitation dynamics and laser action in solutions and films of PPE-PPV copolymer

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We used a variety of ultrafast and steady-state spectroscopy techniques to study the photoexcitation dynamics and laser action in dilute and concentrated solutions and in thin films of *poly(phenylene-ethynylene)/poly(phenylene-vinylene)* [PPE-PPV] copolymer. We found that the primary photoexcitations in PPE-PPV solutions are relatively long-lived singlet excitons with lifetime of about 600 ps, consistent with the high-photoluminescence quantum efficiency. The singlet excitons have *three* distinct photoinduced absorption (PA) bands spanning the mid-IR and near-IR spectral ranges, which are correlated with a strong stimulated emission (SE) band in the blue spectral range. In thin PPE-PPV films, however, the SE band is much weaker because of its overlap with a new PA band that is due to long-lived polaron pairs. As a result we found laser action in dilute PPE-PPV solutions but not in films; this represents the first laser action reported in PPE-type polymers. A study of laser action in solutions of various copolymer concentrations confirms the lack of lasing in concentrated solutions and explains its absence in films. The polaron pair species, triplet excitons that are generated via intersystem crossing, and isolated charged polarons that are generated from polaron pair dissociation are also studied using steady-state spectroscopies.

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I. INTRODUCTION

π-conjugated polymers have become important materials because of their potential applications as active media in organic light emitting diodes (OLED's) (Refs. 1–3) and other optoelectronic devices, such as field effect transistors[4–6] and photovoltaic cells.[7,8] The high photoluminescence (PL) quantum yield of many π-conjugated polymers also makes them promising candidates for active gain media in organic lasers.[9–11] Accordingly laser action has been studied in many π-conjugated polymers in the form of solutions,[12,13] films,[14–19] microcavities,[20–25] and random lasers.[26,27] Two of the most generic π-conjugated polymers for OLED applications are poly(phenylene-vinylene) (PPV) with green emission[1] and poly(phenylene-ethynylene) (PPE) with blue emission;[28] both polymers have relatively high PL quantum efficiency. PPV derivatives have been shown to support laser action in both solutions and films (for a review see Ref. 19). Yet in spite of their high PL quantum efficiency, there is no report of laser action in PPE derivatives. One of the reasons for the absence of lasing in PPE derivatives may be the formation of aggregates with low oscillator strength for light emission to the ground state, which precludes laser action.[29] Recently a PPE-PPV hybrid polymer has been successfully synthesized and was shown to be an excellent active medium for OLED applications.[30] This copolymer contains both PPE and PPV chromophores [see Fig. 1(a)] with a nearly perfect overlap between the emission band of the PPE chromophores and the absorption band of the PPV chromophores, which leads to a very efficient energy migration from PPE to PPV excited states. It is therefore interesting to study the photoexcitation dynamics and laser action of this novel copolymer, in which the well-defined PPV chromophores are isolated from each other by PPE chromophores in the nanometer size dimension.

In this paper we report our study of the ultrafast dynamics of the primary and long-lived photoexcitations and laser action in PPE-PPV copolymers in the form of solutions and thin films. In dilute solutions we found that the primary photoexcitations are singlet excitons with lifetime $\approx$600 ps. The singlet excitons have three associated photoinduced absorption (PA) bands at 0.6 eV, 1.1 eV, and 1.8 eV, respectively, which are correlated with a strong stimulated emission (SE) band in the blue spectral range; all bands have similar dynamics. Laser action in the form of amplified spontaneous emission (ASE) occurs at the 0–1 PL sideband in the blue, at relatively low excitation intensities. In films, however, we found that in addition to the singlet excitons, polaron pairs with a characteristic PA band in the green spectral range are also photogenerated; this was confirmed using steady-state spectroscopy. The PA band of the polaron pair species strongly overlaps with the SE band, thus inhibiting laser action to occur in films. To confirm our findings we studied laser action in PPE-PPV solutions of various concentrations n. We found that in solutions of low concentrations laser action becomes more efficient when n increases; however, at high concentrations laser action becomes increasingly more difficult to generate, in agreement with the absence of laser action in films.

II. EXPERIMENT

The optical properties of the PPE-PPV copolymer in solutions and thin films were investigated by both ps transient and continuous-wave (cw) spectroscopy techniques. We used the ps photomodulation (PM) technique for the main tran-

sient spectroscopy and laser action studies, whereas the absorption, PL, PM, and optically detected magnetic resonance (ODMR) spectra under steady-state conditions were measured using cw techniques.

The transient PM spectrum was studied using the pump-and-probe correlation technique[31] with about 100 fs time resolution. For this study we utilized two fs Ti:sapphire laser systems with low and high repetition rates, having high and low pulse energies, respectively. The low-repetition-rate and high-energy laser system was a homemade Ti:sapphire regenerative amplifier that provides pulses of 100 fs duration at photon energies of 1.55 eV, with 400 μJ energy per pulse at a repetition rate of 1 kHz. The second harmonic of the fundamental pulses at 3.1 eV was used as the pump beam. The probe beam was a white light supercontinuum within the spectral range from 1.6 to 2.8 eV, which was generated using a portion of the Ti:sapphire amplifier output in a 1-mm-thick sapphire plate. To improve the signal-to-noise ratio in our measurements, the pump beam was synchronously modulated by a mechanical chopper at exactly half the repetition rate of the Ti:sapphire laser system ($\cong$500 Hz). The probe beam was mechanically delayed with respect to the pump beam using a computerized translation stage in the time interval t up to 200 ps. The beam spot size on the sample was about 1 mm in diameter for the pump beam and about 0.4 mm diameter for the probe beam. The pump beam intensity was set below 300 μJ/cm^2 per pulse, which is below the signal saturation limit. The wavelength resolution of this system was about 8 nm using a 1/8-m monochromator having a 1.2-mm exit slit, which was placed in the probe beam after it had passed through the sample. The transient spectrum of the photoinduced change (ΔT) in sample transmission (T) was obtained using a phase-sensitive technique with a resolution in $\Delta T/T \approx 10^{-4}$ that corresponds to a photoexcitation density of about 10^{17} cm^{-3}; this is below the threshold exciton density for exciton-exciton annihilation via bimolecular recombination kinetics.[11] In general $\Delta T/T$ is either negative for PA or positive for SE and photobleaching of the optical absorption that originates from the ground state.

The high-repetition-rate and low-energy laser system was an optical parametric oscillator (OPAL, Spectra Physics) that was pumped by a 100 fs Ti:sapphire laser oscillator (Tsunami, Spectra Physics) at a repetition rate of about 80 MHz. The pump beam was extracted directly from the laser oscillator and was frequency doubled to 3.2 eV. The probe beam was extracted from the signal and idler beams of the optical parametric oscillator in the spectral ranges 0.56–0.68 eV and 0.94–1.02 eV, respectively, with about 150 fs time resolution. This laser system provides low-intensity measurements where the pump intensity ranges from 0.1 to 30 μJ/cm^2 per pulse, with $\Delta T/T$ resolution $\approx 10^{-6}$.

For studying laser action at high excitation intensities, which includes spectral narrowing and emission-excitation intensities relation,[25] we used the low-repetition-rate and high-power laser system mentioned above. The excitation pulse was focused through a cylindrical lens forming a narrow strip on a $1\times0.1\times7$ cm^3 cuvette that contained the copolymer solution in toluene. The emission radiation was collected with a 1-mm fiber optic from the side of the cuvette, spectrally analyzed by a 1/2-m spectrometer, detected with a charge coupled device (CCD) camera, and recorded with a PC. The overall spectral resolution of the collecting apparatus was 0.05 nm.

For the cw spectroscopy we used a standard PM setup at 30 K (Ref. 32). The excitation beam was an Ar^+ laser at 353 nm, which was modulated with a mechanical chopper at a frequency of 296 Hz. The probe beam was extracted from a tungsten lamp in the spectral range 0.25–3 eV. A combination of various diffraction gratings, optical filters, and solid-state detectors (silicon, germanium, and indium antimonite) was used to record the PM spectra. The spectral resolution was about 2 nm in the visible spectral range and 4–10 nm in the near-infrared (NIR) range, with $\Delta T/T$ resolution of $\approx 10^{-6}$. This setup was also utilized for measuring the PL spectra, and with some adjustments it was also used for obtaining the ODMR spectrum.

For the ODMR measurements the sample was mounted in a high-Q microwave cavity at 3 GHz equipped with a superconducting magnet.[33] Microwave resonant absorption leads to small changes ΔPL in the PL intensity. By scanning the external magnetic field H the relative change in PL is measured to unravel the magnetic resonance signal for the various photoexcitations. Spin-1/2 species give magnetic resonance at $H_0 \approx 1008$ G, whereas triplet excitons with spin 1 show a relatively sharp magnetic resonance signal at "half-field" below $H_{1/2} = 504$ G. Any deviation from $H_{1/2}$ is proportional to the zero-field-splitting parameters, which can be used to calculate the triplet-wave-function extent;[34] the "full-field" resonance of the triplet excitons[33] was not studied here.

The PPE/PPV copolymer [see Fig. 1(a)] was synthesized by using the procedure reported previously.[30] The polymer had a weight-average molecular weight of 80 000 with a moderate polydispersity index (PDI$\approx$1.4). On the basis of ^{1}H NMR analysis, the vinylene bonds in the copolymer were confirmed to be in the *trans*-configuration ($\sim$92%). For casting the thin films a toluene solution of 6 mg/ml was prepared and the films were spin cast on quartz substrates using a spinner at moderate speed. During the measurements the polymer films were kept at room temperature in an optical cryostat under dynamic vacuum to prevent photo-oxidation; no special precautions were taken for the ps transient and laser action studies of the copolymer solutions.

III. RESULTS AND DISCUSSION

A. Absorption and PL spectra

The room-temperature optical absorption spectra of the PPE-PPV copolymer in solution and film are shown in Fig. 1. The relatively broad absorption band with an onset at 2.8 eV in solution (2.6 eV in the film) that peaks at about 3.2 eV (3.4 eV film) is due to delocalized π-π^* transitions involving optical transitions from the ground state ($1A_g$) to the first odd-parity exciton band ($1B_u$) (Refs. 35 and 36); this band also includes relatively unresolved phonon replicas. The second absorption band at about 4 eV is due to a combination of delocalized and localized π-π^* transitions.[35] There are also two other absorption bands at about 5.2 and 6 eV, which are

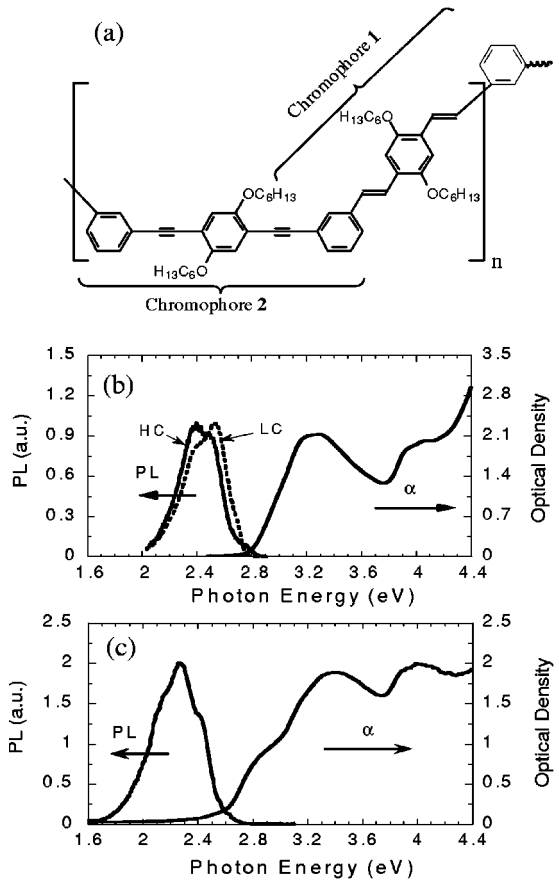

FIG. 1. (a) The backbone structure of the PPE-PPV copolymer; chromophore No. 2 is a PPE moiety, whereas chromophore No. 1 is a PPV moiety. (b) The absorption spectrum (in the form of optical density) and photoluminescence emission spectra of PPE-PPV solutions at low (LC) and high (HC) concentrations. (c) Same as in (b) but for a PPE-PPV film.

not shown here and are mentioned for completeness.[36] In films there are two closely spaced bands at 2.8 and 3.2 eV, respectively, that may be due to either isolated PPV and PPE chromophores or phonon sidebands involving the C-C triple-bond stretching vibration in PPE (≈0.3 eV).

The PL spectra of two solutions with low and high copolymer concentrations and a film are also shown in Fig. 1. The PL band is narrower and the Stokes shift is smaller in solution compared to those in films, and this indicates a narrower distribution of conjugation length in the solutions. However, the PL band in solution is featureless, whereas two phonon replicas (0–1 and 0–2 sideband transitions, respectively) can be discerned in films. Also the PL band in the more highly concentrated solution is more redshifted compared to that of dilute solution; this may be due to self-absorption. It is also interesting to note that the PL band in the PPE-PPV copolymer is blueshifted respect to that of PPV but redshifted respect to PPE; this is consistent with the copolymer backbone structure [Fig. 1(a)]. The overall PL quantum efficiency in the PPE-PPV copolymer is high, reaching about 60% in solution and 50% in films. The latter was measured using an integrating sphere.

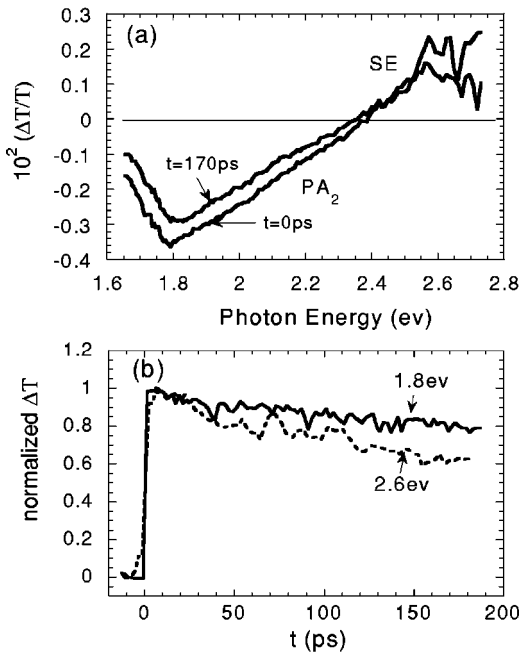

FIG. 2. (a) The ps transient PM spectra of PPE-PPV dilute solution in the visible–near-IR spectral range at delay time $t=0$ and $t=170$ ps, respectively. The photoinduced absorption (PA_2) and stimulated emission (SE) bands are assigned. (b) The transient decay of PA_2 and SE bands up to 200 ps. These results were obtained using the laser amplifier system.

B. Transient response and laser action in PPE-PPV solutions

The ultrafast excitation dynamics in a dilute PPE-PPV solution was studied via the transient PM spectra as shown in Figs. 2 and 3, respectively, for the visible-NIR range (using the laser amplifier system) and mid-IR (using the laser parametric oscillator system) spectral range. Upon excitation at $t=0$ a SE band with maximum at 2.6 eV and three PA bands are instantaneously formed with peaks at 0.6 eV (PA_0) and 1 eV (PA_1) (Fig. 3) and 1.8 eV (PA_2) (Fig. 2), respectively. We found that the SE band is polarized preferentially parallel to the pump beam polarization—i.e., mainly along the copolymer chain direction—and therefore we assign it as due to *intrachain excitons*. This assignment is also in agreement with the apparent similarity between the spectra of SE [Fig. 2(a)] and the cw PL band [Fig. 1(b)]. Figure 2(b) shows that the SE dynamics are similar to those of the three PA bands [Figs. 2(b) and 3(b)]. We thus conclude that the three PA bands and SE band are correlated, and therefore are due to a common species: namely, intrachain excitons. We interpret the three PA bands associated with the intrachain excitons as excited state transitions from the relaxed $1B_u$ exciton to even-parity states (A_g) at higher energies.[37] The lowest-energy band PA_0 is due to the transition $1B_u \rightarrow 2A_g$ (Ref. 38); PA_1 is the transition $1B_u \rightarrow mA_g$ (Ref. 37), where mA_g is the most strongly coupled A_g state to the $1B_u$, whereas PA_2 is the transition $1B_u \rightarrow kA_g$, where kA_g is the most strongly coupled A_g state in another π^*-π band.[37,38] In agreement with our interpretation we note that the measured exciton lifetime of ≈600 ps is consistent with the high PL

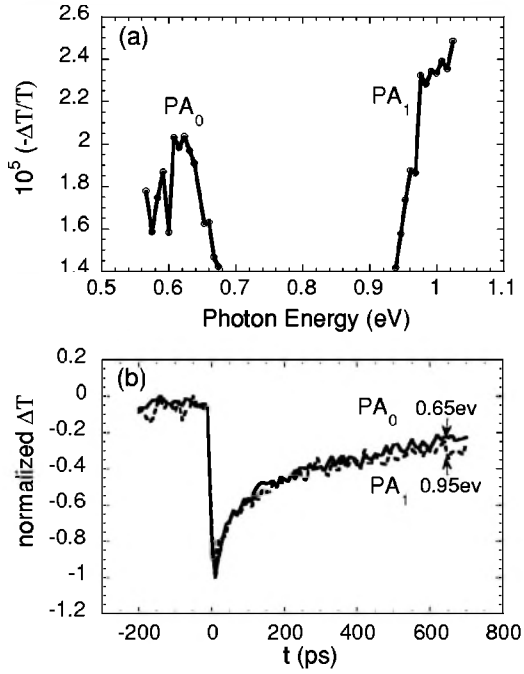

FIG. 3. (a) The ps transient PM spectrum of PPE-PPV dilute solution in the mid-IR spectral range at $t=0$. Two PA bands are assigned (PA_0 and PA_1, respectively). (b) The transient decay of PA_0 and PA_1 up to 700 ps. These results were obtained using the optical parametric oscillator system.

quantum efficiency obtained in PPE-PPV solutions of $\approx$60%, where the exciton radiative time is $\approx$1 ns.

The laser action in the dilute PPE-PPV solution at high excitation intensities I between 1 and 100 μJ/cm^2 is shown in Figs. 4 and 5; to our knowledge this represents the first reported laser action in PPE-type polymers. Figure 4 shows spectral narrowing due to ASE that is concentrated at the 0–1 PL sideband at 2.68 eV. The 0–0 PL band at 2.83 eV is also narrower at high excitation intensities, but is less affected compared to the 0–1 PL sideband. The dependence of the PL bandwidth on I is summarized in Fig. 5. The threshold intensity for ASE occurs at $I_0 \approx 5$ μJ/cm^2, where the emission bandwidth changes from 110 nm to about 8 nm. This dramatic spectral narrowing is completed at $I \approx 8$ μJ/cm^2 and occurs within a relatively narrow intensity range of about 3 μJ/cm^2. Within the same intensity regime the output versus input intensity dependence changes slopes dramatically (Fig. 5), and this also indicates that ASE takes over the PL emission at high intensities.[18] This is also evident by the observation of a narrow laser beam in the blue that comes out from the two sides of the illuminated stripe on the cuvette at $I > I_0$ (Ref. 15).

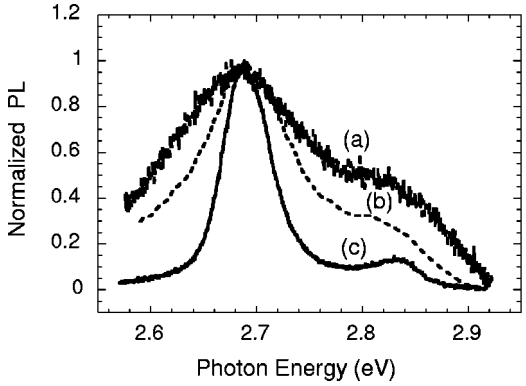

FIG. 4. Laser action in PPE-PPV dilute solution at three different excitation intensities of (a) 2 μJ/cm^2, (b) 5 μJ/cm^2, and (c) 9 μJ/cm^2. Spectral narrowing of both 0-1 and 0-0 PL sidebands is apparent.

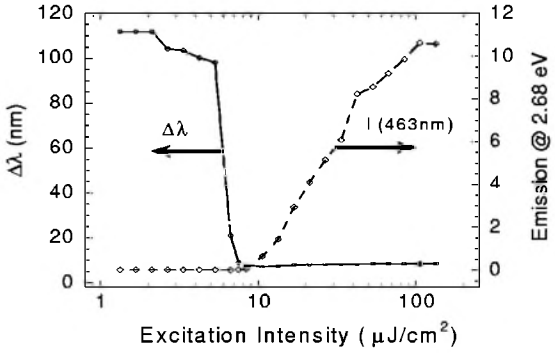

FIG. 5. Spectral narrowing and emission-excitation intensity relation at 2.68 eV in PPE-PPV dilute solution, which shows laser action with threshold intensity of 7 μJ/cm^2.

C. Transient response in PPE-PPV films

The ps transient PM spectra in the visible range and their dynamics are shown in Figs. 6 and 7, respectively, for a PPE-PPV film. Figure 6 shows that in contrast to the PM

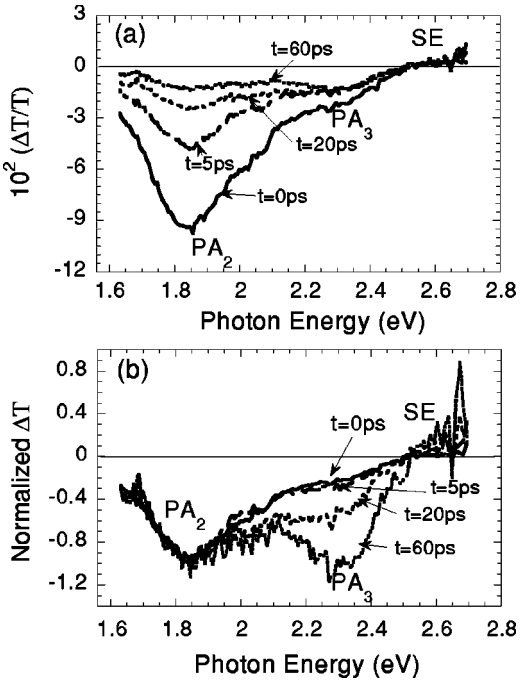

FIG. 6. Transient ps PM spectra of PPE-PPV film in the visible–near-IR spectral range at different delay times (a) and normalized to the spectrum peak at 1.85 eV (b). The SE and PA_2 for excitons and PA_3 for polaron pair excitations are assigned.

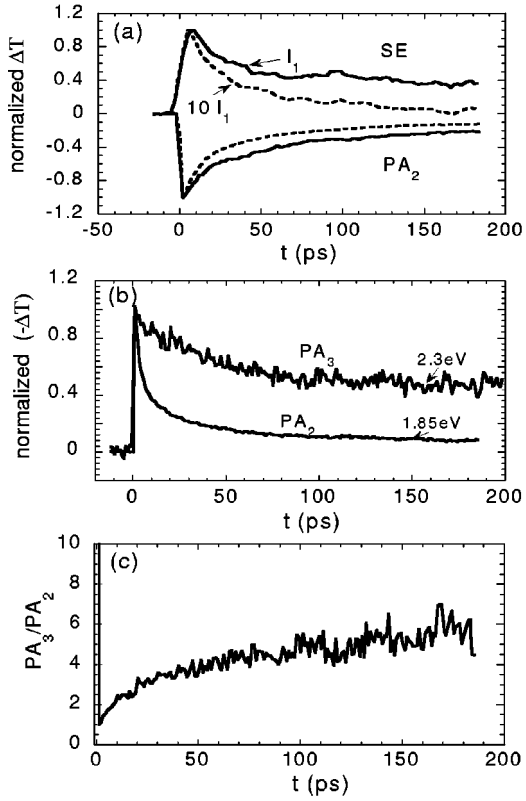

FIG. 7. PM ps transient decays in PPE-PPV film up to 200 ps. (a) SE and PA_2 decays at two different excitation intensities, where I_1 is 23 μJ/cm^2. (b) PA_2 and PA_3 decays. (c) The ratio of PA_3/PA_2 normalized at $t=0$, as a function of delay time.

spectra in the PPE-PPV solution, the PM spectra in the film show a very small SE band above 2.5 eV. With such a weak SE band laser action in PPE-PPV films is not reached; we found neither a spectral narrowing nor a nonlinear emission response in PPE-PPV films at high excitation intensities. Singlet excitons are still photogenerated in the PPE-PPV film as evident from the strong PA_2 band at 1.85 eV, which is similar to that in the solution. However, in addition to PA_2 there is another band PA_3 at about 2.3 eV that competes with the SE band. This new band is better seen in Fig. 6(b), where the PM transient spectra are normalized at 1.85 eV to the spectrum at $t=0$. It is clearly seen that PA_3 gradually becomes the dominant PA band in the transient PM spectrum at $t>100$ ps. The reason for this is the relatively slow dynamics of PA_3, as shown in Fig. 7. The dynamics of PA_2 and SE are the same, showing an exciton lifetime of about 150 ps in film [Fig. 7(a)], which is excitation intensity dependent due to exciton-exciton annihilation. However, PA_3 decay is much longer with a lifetime in the ns time domain [Fig. 7(b)] and does not depend on the excitation intensity. Figure 7(c) shows the relative PA_3/PA_2 strength normalized at $t=0$ as a function of time. It is apparent from the increase in its relative strength that at $t>100$ ps PA_3 becomes the dominant PA band in the PM spectrum, consistent with both Figs. 6(b) and 7(b).

Since PA_3 competes with the SE band, it cannot originate from intrachain excitons that may be trapped in nonradiative

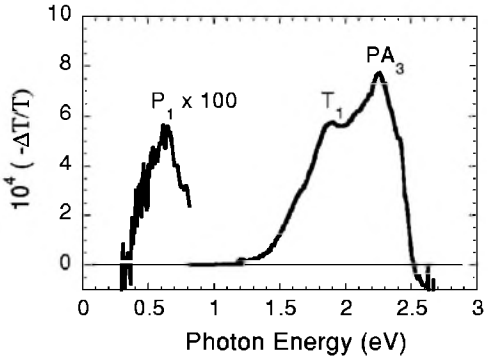

FIG. 8. The steady-state PM spectrum of PPE-PPV film at 30 K measured at 296 Hz and excited with the 353-nm plasma line of an Ar^+ laser at an intensity of 1 W/cm^2. Various PA bands are assigned; P_1 is for polaron excitations, T_1 is for triplet excitons, and PA_2 is for long-lived polaron-pair excitations.

recombination centers, because the SE process would affect them too. We thus conjecture that PA_3 originate from a species with very small oscillator strength of radiative transition to the ground state. Such species are formed when the photogenerated oppositely charged polarons do not strongly overlap.[39] This may occur for interchain excitons or polaron pairs (PP's), where the oppositely charged geminate polarons reside on adjacent chains, but are still coulombically bound together, or for intrachain PP's, where the geminate polarons reside on the same chain but their wave functions do not strongly overlap. This might be caused, for example, by an intrachain defect that separates the geminate polarons to reside on different chain segments.[40] We therefore conclude that PA_3 is due to interchain or intrachain PP excitations. Intrachain PP excitations may decay faster than interchain PP excitations; in fact, the PP excitations may have a broad distribution of lifetimes. We ascribe the ns PA_3 decay to the intrachain PP excitations; interchain PP excitations may decay much slower. These species may become trapped with low-temperature lifetimes in the millisecond time domain. In this case we can investigate their properties using the cw PM technique at low temperatures,[41] as discussed below.

D. Steady-state PM spectroscopy of PPE-PPV films

Figure 8 shows the cw PM spectrum of a PPE-PPV film at 80 K. Two PA bands in the visible-NIR spectral range, which are not completely spectrally resolved, dominate the PM spectrum. Among them the lower-energy PA band peaks at $\approx$1.85 eV, whereas the higher-energy PA band peaks at $\approx$2.25 eV. The PM also contains photobleaching of the π-π^* transitions starting from 2.5 eV. In addition there is a third, very small PA band that peaks at $\approx$0.6 eV; in fact this PA band is smaller than the other two PA bands by about two orders of magnitude.

It is tempting to assign the higher-energy PA band at 2.3 eV (Fig. 8) as due to the long-lived PA_3 components, which become prominent in the transient PM spectrum in the ns time domain. In fact, from measurements of its frequency dependence, which starts falling off at about 1 kHz (not shown here) we conclude that this cw band is indeed due to

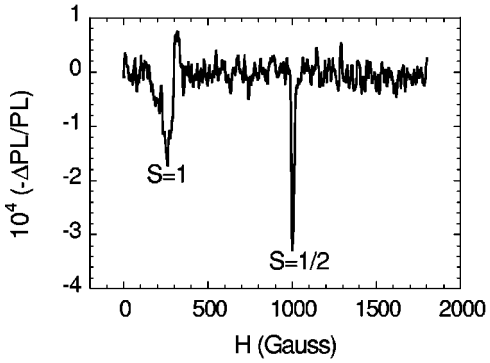

FIG. 9. The PL-ODMR spectrum of PPE-PPV that is presented in the form of relative change in the PL emission (ΔPL/PL) as a function of the external magnetic field H. $S=1$ signal at $H_{1/2} \approx 250$ G is the "half-field" resonance of triplet excitons at $g \approx 8$; the $S=1/2$ signal at $H_0=1008$ G is a spin-1/2 resonance of polaron excitations at $g \approx 2$.

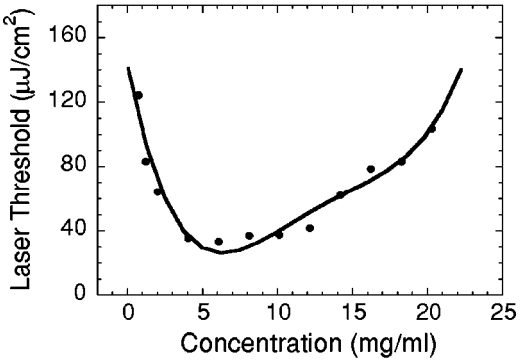

FIG. 10. The laser threshold intensity in PPE-PPV toluene solutions of different copolymer chain concentrations. The threshold intensity saturates at intermediate concentrations and is not measurable at concentrations higher than 20 mg/ml.

long-lived photoexcitations. In addition from its linear intensity dependence (not shown here) we conclude that it has monomolecular recombination kinetics. From the peak photon energy, recombination kinetics, and long lifetime we conjecture that the higher-energy PA band is indeed due to PP excitations.[39–41]

The lower-energy PA band at 1.85 eV (Fig. 8) cannot be due to singlet excitons, even that it peaks at the same photon energy as that of the characteristic PA_2 band of singlet excitons, as found above in our ps transient PM studies described in Sec. III B. The reason for this is that the cw lower-energy PA band does not have an accompanying PA band in the mid-IR spectral range, such as PA_0 or PA_1, that accompany PA_2 of singlet excitons (see Sec. III B). From its peak photon energy position we speculate that this cw PA band is due to triplet excitons.[42] Singlet excitons may change their spin state to the triplet manifold via the intersystem crossing process. This process is relatively weak in π-conjugated polymers, with a rate of about 5×10^8/sec (Ref. 43), but is still present in the copolymer chains. The PL-ODMR spectrum shown in Fig. 9 is in agreement with this interpretation. It shows a prominent resonance at low temperature at $H_{1/2} \approx 250$ G, which is consistent with triplet excitons having $S=1$ and "half-field" resonance at $g \approx 8$. From the magnetic field position of the "half-field" resonance we calculate that the triplet excitons have a relatively large axial zero-field-splitting parameter of ≈280 G. This is similar to the axial zero-field-splitting parameter of triplets in PPV, from which it was previously calculated that their wave-function extent is ≈3.2 Å (Ref. 34). We therefore conclude that the triplet excitons in PPE-PPV are in fact extremely localized, probably on the benzene ring in the chain backbone.

The peak position of the weakest PA band in the PM spectrum (Fig. 8) is ≈0.6 eV, similar to that of charged polarons in PPV (Ref. 34). We therefore speculate that it is due to separated charged polaron excitations. A small fraction of the PP excitations may dissociate at long times into separated polarons. This is evident from this band intensity, which is smaller than the other PA bands in the PM spectrum by a factor of about 100 (Fig. 8). The PL-ODMR resonance at $H=1008$ G (Fig. 9) is consistent with this interpretation. This resonance is due to spin 1/2 at $g \approx 2$ in agreement with the polaron interpretation. PP excitations are spin-singlet species and thus cannot give a strong PL-ODMR resonance.[41] The spin-1/2 resonance thus shows that long-lived separated polarons are also photogenerated in the copolymer film and the weak PA band in the mid-IR spectral range is the only candidate for these species.

E. Laser action study in solutions

As mentioned above we found laser action in dilute solutions of the PPE-PPV copolymer but not in PPE-PPV films. The reason for the lack of laser action in copolymer films may be the PP excitations with a PA band that overlaps with the SE band. To verify this interpretation and see whether the PP excitations are intrachain or interchain in nature, which in principle can form in concentrated solutions, we studied the laser action in a series of copolymer solutions in toluene with various concentrations n. The threshold excitation intensity I_0 for the ASE was obtained for each solution from the emission-excitation intensity relation. Figure 10 summarizes our findings for the ASE threshold versus n.

At low concentrations I_0 dramatically decreases with n. This can be explained as follows. For laser action to occur the optical gain g has to overcome the optical loss α_L at the lasing wavelength: namely, $\alpha_L \leqslant g$. At low gain, g is given by $N\sigma_g$, where N is the photogenerated exciton density in the solution and σ_g is the optical gain cross section at the lasing wavelength. The photogenerated exciton density N, in turn, is proportional to the absorbed photons and can be written as

$$N=(I/h\nu)[1-\exp(-\alpha d)], \tag{1}$$

where $h\nu$ is the photon energy at the excitation wavelength and αd is the solution optical density in the cuvette. The polymer optical density αd is given by the relation $n\sigma d$, where σ is the polymer absorption cross section at the excitation wavelength. Since αd is small, we can expand the exponential in Eq. (1) in Taylor series and take only the first

two terms. Combining the all of the above relations we then write the excitation threshold intensity I_0 for lasing at low n as

$$I_0 = \alpha_L/(n\sigma_g\sigma d), \quad (2)$$

which can explain the decrease in I_0 seen in Fig. 10 at low n ($n<5$ mg/ml).

However, at concentrations $n\approx 5$ mg/ml, I_0 saturates and starts increasing again at larger n. At $n>20$ mg/ml it was not possible to reach laser action anymore even at very high excitation intensities. The dependence of I_0 on n at large n is thus in agreement with the obtained laser action in dilute solutions and its absence in films as found above. The dependence on n shows that concentrated solutions support PP excitations that interfere with laser action. We therefore conclude that the PP excitations are mainly interchain, since otherwise even low-n solutions would have only shown weak lasing, or not at all.

IV. CONCLUSIONS

We studied photoexcitation dynamics and laser action in solutions and thin films of PPE-PPV copolymer. In dilute solutions we found that the primary photoexcitations are singlet excitons with a lifetime of about 600 ps, which are characterized by three correlated PA bands in the visible-NIR and mid-IR spectral ranges and a SE band in the visible range. At high excitation intensities the strong SE band gives rise to laser action in the form of ASE, where the emission spectrum dramatically narrows down from $\approx$110 nm to 8 nm at a threshold intensity of ≈ 7 μJ/cm^2. In addition to singlet excitons, PPE-PPV films also support PP excitations that are characterized by a PA band in the visible range that overlaps with the SE band. This dramatically weakens the SE band and does not allow ASE to develop in films even at very high excitation intensities. From the study of laser action in toluene solutions of various copolymer concentrations we confirm that laser action is absent at high concentrations, which approaches the chromophore concentrations in films. The laser study in solutions indicates that the photoinduced PP excitations are mainly interchain in nature. These excitations have a very broad lifetime distribution that allows their observation in cw PM spectroscopy at low temperature. In PPE-PPV films we also confirmed the existence of long-lived PP photoexcitations that are spin singlet, triplet excitons with spin 1, and isolated polaron excitations with spin 1/2 by steady-state PM and PL-ODMR spectroscopies.

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